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(54) Nitrogen trifluoride as an in-situ cleaning agent

(57) Chemical vapor deposition hardware and semiconductor wafers are cleaned utilizing nitrogen trifluoride as an etching agent wherein the nitrogen trifluoride is introduced into a heated chemical vapor deposition reactor under a partial pressure for a period of time sufficient to clean the deposited film of material. The etching agent and method of etching is suitable to remove substantially all deposited quantities of silicon nitride, polycrystalline silicon, titanium silicide, tungsten silicide, refractory metals and their silicides.

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SPECIFICATION

Nitrogen trifluoride as an in-situ cleaning agent and method for cleaning boats and tubes using nitrogen trifluoride

This invention relates generally a cleaning agent and method of cleaning boats and tubes used in wafer fabrication facilities. More particularly, the present invention relates to the use of nitrogen trifluoride as a cleaning agent for cleaning silicon nitride and polycrystalline silicon films from boats and tubes used in the chemical vapor deposition of semiconductor wafers. Further, the present invention relates to a method of cleaning residual silicon films from boats and tubes used in semiconductor wafer fabrication facilities.

Boats, tubes and other associated quartz hardware used in the chemical vapor deposition fabrication of semiconductor wafers become contaminated by polycrystalline silicon, silicon nitride, tungsten, titanium or other material which is deposited upon the wafer substrate during a chemical vapor deposition run. To insure accurate and unadulterated chemical vapor deposition onto a substrate it is necessary to clean or etch adulterating substances from the boats, tubes and other quartz hardware used in the fabrication of semiconductor wafers. However, several serious problems exist with conventional cleaning agents and methods for cleaning the boats, tubes and other quartz hardware used in chemical vapor deposition fabrication facilities.

Conventional cleaning or etching agents and methods require that the chemical vapor deposition tube be removed from the production line for cleaning. Removal of the tube is not only time consuming but also increases production costs. The tube, boats and other quartzware is then cleaned with acids, generally used, acids consist of hydrofluoric acid, nitric acid, hydrochloric acid, or phosphoric acid. These cleaning agents necessitate wet cleaning techniques which present substantial health, safety and environmental concerns. Moreover, due to the high temperatures generated in the fabrication facility during a deposition run, conventional cleaning or etching agents and methods require long periods of time to permit the quartz hardware to cool before cleaning may begin.

Therefore, it has been found desirable to provide a cleaning agent for in-situ cleaning of the deposition tube and associated hardware. An in-situ cleaning method would eliminate substanially all of the non-production time associated with conventional cleaning agents and cleaning methods as well as the health, safety and environmental hazards associated with handling conventional acid cleaning agents.

Accordingly, it is an object of the present invention to provide a cleaning or etching agent for in-situ cleaning of chemical vapor deposition apparatus tubes, boats and associated quartz hardware.

It is another object of the present invention to provide a method for the in-situ cleaning or etching of chemical vapor deposition apparatus tubes, boats and associated quartz hardware.

It is still another object of the present invention to provide a cleaning or etching agent for in-situ cleaning which eliminates the necessity of using wet cleaning techniques.

It is yet another object of the present invention to provide a method of in-situ cleaning which eliminates the necessity of using wet cleaning techniques.

It is a further object of the present invention to employ nitrogen trifluoride as a cleaning or etching agent for in-situ cleaning of chemical vapor deposition apparatus tubes, boats and associated quartz hardware.

It is a still further object of the present invention to provide a method of cleaning or etching of chemical vapor deposition apparatus tubes, boats and associated quartz hardware employing nitrogen trifluoride as a cleaning or etching agent.

It is yet a further object of the present invention to provide a cleaning or etching agent which will remove silicon nitride, polycrystalline silicon, titanium, tungsten and other materials deposited onto semiconductor wafers in a chemical vapor deposition apparatus.

It is another object of the present invention to provide a cleaning or etching agent and method which will remove silicon nitride, polycrystalline silicon, titanium, tungsten and other materials deposited onto semiconductor wafers in a chemical vapor deposition apparatus without removing the underlying wafer substrate.

It is still another object of the present invention to employ nitrogen trifluoride as a cleaning or etching agent for in-situ removal of silicon nitride, polycrystalline silicon, titanium, tungsten and other materials deposited onto semiconductor wafers in a chemical vapor deposition apparatus.

It is yet another object of the present invention to provide a method of in-situ cleaning or etching employing nitrogen trifluoride for the removal of silicon nitride, polycrystalline silicon, titanium, tungsten and other materials deposited onto semiconductor wafers in a chemical vapor deposition apparatus.

These and other objects, features and advantages hereinafter disclosed will be more apparent from the following more detailed description of the preferred embodiment of the present invention.

According to the present invention there is provided a cleaning or etching agent for etching silicon nitride, polycrystalline silicon, titanium, tungsten or other materials typically deposited onto semiconductor wafers during a chemical vapor deposition run, comprising nitrogen trifluoride. The chemical vapor deposition tube, boats and associated quartz hardware used in growing silicon nitride, polycrystalline silicon, tungsten or titanium silicide or other refractory metals or their silicides and other films may be cleaned by the nitrogen trifluoride in their respective deposition chambers without necessitating their time consuming removal.

This in-situ cleaning provides for cleaner reaction chambers, and the nitrogen trifluoride, which is a gas at ambient temperatures, may be used with chemical vapor deposition equipment used in wafer fabrication. Further, the in-situ cleaning of tubes, boats and associated hardware used in the chemical vapor deposition growth of silicon nitride, polycrystalline silicon, tungsten or titanium silicide or other refractory metals or their silicides may be performed without the assistance of a plasma.

Significantly, it has been found that nitrogen trifluoride etching, unlike conventional wet etch techniques, presents little or no attack on any quartz hardware. Typical levels of nitrogen trifluoride attack on the quartz hardware have been found to be 5–10 Å/min. This significant reduction in the degree of attack on the quartz hardware, as compared to the conventional wet etch techniques, serves to extend the useful life of the hardware as well as maintain the critical dimensions of the quartz hardware. More significantly, perhaps, nitrogen trifluoride cleaning of the deposition chamber tube generates fewer foreign particles which results in a cleaner film growth onto the wafer substrate during a deposition run.

According to a preferred embodiment of the present invention there is provided a method of cleaning tubes, boats and associated quartz hardware used in chemical vapor deposition. According to this method after a deposition run nitrogen trifluoride is introduced into an evacuated chemical vapor deposition reaction tube at a temperature exceeding 350°C. All quartz hardware required to grow a film of silicon nitride or polycrystalline silicon may also be loaded into the reaction tube. The reaction tube is back-filled to a pressure of 300–600 Torr and allowed to soak for a period of time sufficient to clean the tube and any quartz hardware introduced into the tube. Residual nitrogen trifluoride gases are removed from the reaction tube by purging the tube with nitrogen. After purging, the reaction tube may be opened, the cleaned quartz hardware removed and the reactor may be made ready for the next deposition run.

EXAMPLE 1

A quartz boat having 5–6 microns silicon nitride and polycrystalline silicon was placed into a very dirty chemical vapor deposition tube at 380°C. The tube was evacuated to 0.00 Torr and backfilled with NF_3 to 400 Torr and allowed to soak for fifteen minutes. The tube was then pumped to base, purged with N_2 and backfilled with nitrogen. The boat was removed from the reactor and visual inspection revealed that it was totally clean except for some cobweb-like film. This web-like film was believed to be some unetchable oxide. The etch rate was found to be about 85 Å/min.

EXAMPLE 2

Silicon oxide semiconductor wafers having approximately a 2 micron layer of polycrystalline silicon were placed into the chemical vapor deposition reactor. The same procedures were followed as in Example 1. Again the polycrystalline silicon was removed down to the silicon oxide layer of the wafer substrate. The substrate was attacked only where there were pinholes in the silicon oxide or where the oxide was thought to be non-existent under the polycrystalline silicon. The etch rate was found to be about 500 Å/min.

EXAMPLE 3

The same procedures as in Examples 2 and 3 above, were followed except that both the temperature was varied between 380°C and the 500°C and the pressure was varied between 200 and 600 Torr. Visual inspection of the substrates and apparatus tested revealed that almost all of the silicon nitride or polycrystalline silicon had been cleaned. The etch rates were found to vary exponentially with increased temperature and pressure. The etch rates were as follows:

Silicon Nitride

Temperature (°C)	Pressure (Torr)	Etch Rate (Å/min)
380	200	23
380	400	85
380	600	165
425	200	155
425	400	662
425	600	1275
500	200	430
500	400	1840
500	600	4675

Polycrystalline Silicon

Temperature (°C)	Pressure (Torr)	Etch Rate (Å/min)
380	200	320
380	400	490
380	600	1550
425	200	1600
425	400	5500
425	600	15000
500	200	1800
500	400	13000
500	600	57000

The chemical reactions of the present invention proceed substantially as follows:

$$2\ NF_3 \xrightarrow{>350°C} NF_2{-}NF_2+F_2$$
$$F_2+Si_xN_y \longrightarrow SiF_4\uparrow+N_2\uparrow$$
$$2\ F_2+Si \longrightarrow SiF_4\uparrow$$

It is important to note that both nitrogen trifluoride and its by-product N_2F_4 are highly toxic and explosive under pressure or upon contact with reducing agents. However, since they would be used at reduced pressure and/or at low concentrations, this should not be considered a problem with the present invention.

There is, therefore, provided a new etchant gas and method of in-situ cleaning of chemical vapor deposition tubes, boats and associated quartz hardware which provides a quick and efficient method of cleaning quartz hardware used in chemical vapor deposition of semiconductor wafers.

While the invention has been particularly shown and described in reference to the preferred embodiments thereof, it will be understood by those skilled in the art that changes in form and details may be made therein without departing from the spirit and scope of the invention. For instance, much lower pressures (and flowing of NF_3 continuously) can be used to accomplish the same result, although the etch rates will be somewhat lower than in Example 3.

CLAIMS

1. An etching agent for removing deposited materials from chemical vapor deposition hardware, comprising nitrogen trifluoride.
2. The etching agent according to Claim 1, wherein said deposited material comprises silicon nitride.
3. The etching agent according to Claim 1, wherein said deposited material comprises polycrystalline silicon.
4. The etching agent according to Claim 1, wherein said deposited material comprises a

titanium silicide.

5. The etching agent according to Claim 1, wherein said deposited material comprises a tungsten silicide.

6. The etching agent according to Claim 1, wherein said deposited material comprises a refractory metal.

7. The etching agent according to Claim 1, wherein said deposited material comprises a refractory metal silicide.

8. A method of cleaning chemical vapor deposition hardware, comprising the steps of:

providing a chemical vapor deposition reactor having a quartz reactor tube, said reactor tube further having a film of material deposited thereon;

heating said reactor to a temperature sufficient to permit cleaning of said film of material;

evacuating said reactor;

introducing said nitrogen trifluoride into said reactor at a positive pressure and for a sufficient time to permit cleaning of said film of material; and

purging said reactor of said nitrogen trifluoride.

9. The method of cleaning chemical vapor deposition hardware according to Claim 8, wherein said step of providing a chemical vapor deposition reactor further comprises the step of:

introducing boats or other quartz chemical vapor deposition hardware having a film of a material thereon into said reactor.

10. The method of cleaning chemical vapor deposition hardware according to Claim 8, wherein said film of a material further comprises silicon nitride.

11. The method of cleaning chemical vapor deposition hardware according to Claim 8, wherein said film of a material further comprises polycrystalline silicon.

12. The method of cleaning chemical vapor deposition hardware according to Claim 8, wherein said film of a material further comprises titanium silicide.

13. The method of cleaning chemical vapor deposition hardware according to Claim 8, wherein said film of a material further comprises tungsten silicide.

14. The method of cleaning chemical vapor deposition hardware according to Claim 8, wherein said film of a material further comprises a refractory metal.

15. The method of cleaning chemical vapor deposition hardware according to Claim 8, wherein said film of a material further comprises a refractory metal silicide.

16. The method of cleaning chemical vapor deposition hardware according to Claim 9, wherein said film of a material further comprises silicon nitride.

17. The method of cleaning chemical vapor deposition hardware according to Claim 9, wherein said film of a material further comprises polycrystalline silicon.

18. The method of cleaning chemical vapor deposition hardware according to Claim 9, wherein said film of a material further comprises titanium silicide.

19. The method of cleaning chemical vapor deposition hardware according to Claim 9, wherein said film of a material further comprises tungsten silicide.

20. The method of cleaning chemical vapor deposition hardware according to Claim 9, wherein said film of a material further comprises a refractory metal.

21. The method of cleaning chemical vapor deposition hardware according to Claim 9, wherein said film of a material further comprises a refractory metal silicide.

22. The method of cleaning chemical vapor deposition hardware according to Claim 8, wherein said reactor is heated to a temperature no less than about 350°C.

23. The method of cleaning chemical vapor deposition hardware according to Claim 9, wherein said reactor is heated to a temperature no less than about 350°C.

24. The method of cleaning chemical vapor deposition hardware according to Claim 8, wherein said positive pressure is no greater than about 600 Torr.

25. The method of cleaning chemical vapor deposition hardware according to Claim 9, wherein said positive pressure is no greater than about 600 Torr.

26. The method of cleaning chemical vapor deposition hardware according to Claim 8, wherein said reactor is evacuated to about 0.00 Torr.

27. The method of cleaning chemical vapor deposition hardware according to Claim 9, wherein said reactor is evacuated to about 0.00 Torr.

28. The method of cleaning chemical vapor deposition hardware according to Claim 8, wherein said purging step further comprises the steps of:

pumping said reactor to base pressure; purging said reactor with nitrogen gas; and backfilling said reactor with nitrogen gas.

29. The method of cleaning chemical vapor deposition hardware according to Claim 8, wherein said purging step further comprises the steps of:

pumping said reactor to base pressure; purging said reactor with nitrogen gas; and backfilling said reactor with nitrogen gas.

30. A method of cleaning semiconductor wafers, comprising the steps of:

providing a chemical vapor deposition reactor; introducing semiconductor wafers having a film

of a material to be cleaned;
heating said reactor to a temperature sufficient to permit cleaning of said film of material;
evacuating said reactor;
introducing nitrogen trifluoride into said reactor at a positive pressure and for a sufficient time to permit cleaning of said film of material; and
purging said reactor of said nitrogen trifluoride.

31. The method of cleaning semiconductor wafers according to Claim 30, wherein said step of providing a chemical vapor deposition reactor further comprises the step of:
introducing boats or other quartz chemical vapor deposition hardware having a film of a material thereon into said reactor.

32. The method of cleaning semiconductor wafers according to Claim 30, wherein said film of a material further comprises silicon nitride.

33. The method of cleaning semiconductor wafers according to Claim 30, wherein said film of a material further comprises polycrystalline silicon.

34. The method of cleaning semiconductor wafers according to Claim 30, wherein said film of a material further comprises titanium silicide.

35. The method of cleaning semiconductor wafers according to Claim 30, wherein said film of a material further comprises tungsten silicide.

36. The method of cleaning semiconductor wafers according to Claim 30, wherein said film of a material further comprises a refractory metal.

37. The method of cleaning semiconductor wafers according to Claim 30, wherein said film of a material further comprises a refractory metal silicide.

38. The method of cleaning semiconductor wafers according to Claim 31, wherein said film of a material further comprises silicon nitride.

39. The method of cleaning semiconductor wafers according to Claim 31, wherein said film of a material further comprises polycrystalline silicon.

40. The method of cleaning semiconductor wafers according to Claim 31, wherein said film of a material further comprises titanium silicide.

41. The method of cleaning semiconductor wafers according to Claim 31, wherein said film of a material further comprises tungsten silicide.

42. The method of cleaning semiconductor wafers according to Claim 31, wherein said film of a material further comprises a refractory metal.

43. The method of cleaning semiconductor wafers according to Claim 31, wherein said film of a material further comprises a refractory metal silicide.

44. The method of cleaning chemical vapor deposition hard according to Claim 30, wherein said reactor is heated to a temperature no less than about 350°C.

45. The method of cleaning semiconductor wafers according to Claim 31, wherein said reactor is heated to a temperature no less than about 350°C.

46. The method of cleaning semiconductor wafers according to Claim 30, wherein said positive pressure is no greater than about 600 Torr.

47. The method of cleaning semiconductor wafers according to Claim 31, wherein said positive pressure is no greater than about 600 Torr.

48. The method of cleaning semiconductor wafers according to Claim 30, wherein said reactor is evacuated to about 0.00 Torr.

49. The method of cleaning semiconductor wafers according to Claim 31, wherein said reactor is evacuated to about 0.00 Torr.

50. The method of cleaning semiconductor wafers according to Claim 30, wherein said purging step further comprises the steps of:
pumping said reactor to base pressure; purging said reactor with nitrogen gas; and backfilling said reactor with nitrogen gas.

51. The method of cleaning semiconductor wafers according to Claim 31, wherein said purging step further comprises the steps of:
pumping said reactor to base pressure; purging said reactor with nitrogen gas; and backfilling said reactor with nitrogen gas.

52. An etching agent substantially as hereinbefore described.

53. The method of cleaning vapor deposition hardware substantially as hereinbefore described with reference to and as illustrated by the examples set forth.

54. The method of cleaning semiconductor wafers substantially as hereinbefore described with reference to and as illustrated by the examples set forth.

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